

CLAIMS

1. Porous hydrophilic membranes comprising a porous inert support on which an ionomer is deposited, said membranes being characterized in that they have a water permeability higher than 1 l/(h.m².Atm), preferably higher than 10 l/(h.m².Atm), more preferably higher than 100 l/(h.m².Atm), still more preferably higher than 500 l/(h.m².Atm); the ionomer being under amorphous form and having the hydrophilic group in the acid form.
2. Membranes according to claim 1, having pores partially or totally occluded to gases.
3. Membranes having pores totally occluded to gases according to claims 1-2, containing an ionomer amount higher than about 30% by weight.
4. Membranes having pores partially occluded to gases according to claims 1-2, containing an ionomer amount lower than about 20% by weight.
5. Membranes according to claims 1-4, wherein the porous support is formed by (per)fluoropolymers, preferably PTFE, still more preferably bistretched PTFE.
6. Membranes according to claims 1-5, wherein the ionomers are (per)fluorinated polymers and they preferably have SO₃H and/or -COOH, preferably SO₃H, functionality, and an equivalent weight such as to result amorphous.

7. Membranes according to claim 6, wherein the ionomers comprise:

- (A) monomeric units deriving from one or more fluorinated monomers containing at least an ethylene unsaturation;
- (B) fluorinated monomeric units containing functional groups transformable into hydrophilic groups, preferably $-\text{SO}_2\text{F}$ and/or $-\text{COOR}$, $-\text{COF}$, wherein R is a $\text{C}_1\text{-C}_{20}$ alkyl radical or a $\text{C}_6\text{-C}_{20}$ aryl radical, in such an amount as to give the above equivalent weight, the functional groups being converted into hydrophilic groups, preferably into $-\text{SO}_3\text{H}$ and/or $-\text{COOH}$ groups in the final membrane if the functional groups were $-\text{SO}_2\text{F}$ and/or $-\text{COOR}$, $-\text{COF}$.

8. Membranes according to claim 7, wherein the fluorinated monomers of type (A) are selected from the following:

- vinylidene fluoride (VDF);
- $\text{C}_2\text{-C}_8$ perfluoroolefins, preferably tetrafluoroethylene (TFE);
- $\text{C}_2\text{-C}_8$ chloro- and/or bromo- and/or iodo-fluoroolefins, such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene;
- $\text{CF}_2=\text{CFOR}_f$ (per)fluoroalkylvinylethers (PAVE), wherein R_f is a $\text{C}_1\text{-C}_8$ (per)fluoroalkyl, for example trifluo-

romethyl, bromodifluoromethyl, pentafluoropropyl;

- $\text{CF}_2=\text{CFOX}$ perfluoro-oxyalkylvinylethers, wherein X is a C_1 - C_{12} perfluoro-oxyalkyl having one or more ether groups, for example perfluoro-2-propoxy-propyl.

9. Membranes according to claims 7-8, wherein the fluorinated monomers of type (B) are selected from the following:

- $\text{F}_2\text{C}=\text{CF}-\text{O}-\text{CF}_2-\text{CF}_2-\text{SO}_2\text{F}$;
- $\text{F}_2\text{C}=\text{CF}-\text{O}-[\text{CF}_2-\text{CXF}-\text{O}]_n-\text{CF}_2-\text{CF}_2-\text{SO}_2\text{F}$

wherein X = Cl, F or CF_3 ; n = 1-10;

- $\text{F}_2\text{C}=\text{CF}-\text{O}-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{SO}_2\text{F}$
- $\text{F}_2\text{C}=\text{CF}-\text{Ar}-\text{SO}_2\text{F}$ wherein Ar is an aryl ring;
- $\text{F}_2\text{C}=\text{CF}-\text{O}-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{COF}$
- $\text{F}_2\text{C}=\text{CF}-\text{O}-[\text{CF}_2-\text{CXF}-\text{O}]_n-\text{CF}_2-\text{CF}_2-\text{COF}$

wherein X = Cl, F or CF_3 ; n = 1-10.

10. Membranes according to claims 1-9, wherein the ionomers contain from 0.01 to 5% by moles of monomeric units deriving from a bis-olefin of formula:



wherein:

m = 2-10, preferably 4-8;

R_1 , R_2 , R_3 , R_6 , equal to or different from each other, are H or C- C_5 alkyl groups.

11. Membranes according to claims 1-10, wherein the ionomers comprise:

- monomeric units deriving from TFE;
- monomeric units deriving from $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$;
- monomeric units deriving from the bis-olefin of formula (I);
- iodine atoms in end position.

12. Membranes according to claims 1-11, wherein the amorphous ionomer shows a substantial absence of crystallinity.
13. Membranes according to claims 1-11, wherein the amorphous ionomer has a residual crystallinity lower than 5%, preferably lower than 1%.
14. Membranes according to claims 1-13, wherein the (per)fluorinated ionomers are crosslinked.
15. Membranes according to claims 1-13, containing one or more amorphous or crystalline (per)fluoropolymers, the amorphous ones being different from the ionomer used in the membrane.
16. Membranes according to claim 15, wherein the (per)fluoropolymers are of crystalline ionomeric type.
17. Use of the membranes according to claims 1-16 in separation processes, preferably in microfiltration and ultrafiltration processes of aqueous solutions, and in pervaporation processes.
18. Use according to claim 17, wherein the membranes are those of claim 3 in iperfiltration and reverse osmosis

processes.

19. A process for preparing hydrophilic porous membranes according to claims 1-16, comprising a porous support formed by a (per)fluorinated polymer, and amorphous (per)fluorinated ionomers containing hydrophilic groups, preferably having $-SO_3H$ or $-COOH$ functionality, said process comprising the following steps:

a) impregnation of the porous support formed by the (per)fluorinated polymer, with a (per)fluorinated ionomer having hydrolyzable groups, preferably $-SO_2F$, $-COOR$, $-COF$, wherein R is a C_1-C_{20} alkyl radical or a C_6-C_{20} aryl radical, using a solution of the ionomeric compound in fluorinated organic solvent at a concentration in the range 1-20% by weight, preferably 4-20% by weight till obtaining a membrane having the pores substantially filled by the ionomeric solution, the impregnation is carried out at temperatures comprised between the room temperature and $120^\circ C$, preferably between $15^\circ C$ and $40^\circ C$; the so impregnated membrane is subjected to thermal treatment at temperatures from 50° to $200^\circ C$, preferably from 120° to $160^\circ C$ till substantial removal of the solvent and obtainment of a substantially transparent membrane, optionally step a)

is repeated until the membrane appears substantially transparent;

- b) treatment of the membrane obtained in a) with inorganic strong, preferably aqueous, alkali, i.e. bases which are completely dissociated in water, to obtain the conversion of the functional groups into hydrophilic groups, preferably from $-\text{SO}_2\text{F}$ into $-\text{SO}_3^-$, and of the $-\text{COOR}$, $-\text{COF}$ groups into $-\text{COO}^-$ groups;
 - c) treatment of the membrane obtained in b) with inorganic strong acids, i.e. acids which are completely dissociated in aqueous solution, obtaining the (per)fluorinated ionomer in acid hydrophilic form;
 - d) optionally treatment with water at temperatures in the range 50°C - 100°C , in case repeated, until removal of the ionomer in excess and neutral pH of the washing waters.
20. A process according to claim 19, wherein in step a) the solvent has a boiling point at room pressure lower than 180°C , preferably lower than 120°C .
21. A process according to claims 19-20, wherein in step b) the used strong alkalis are the hydroxides of the Group Ia metals.
22. A process according to claims 19-21, wherein at the end of step b) washings with water are carried out until a

neutral pH of the washing waters is obtained.

23. A process according to claims 19-22, wherein the ionomer is crosslinked by adding to the impregnation solution a) crosslinking agents.
24. A process according to claim 23, wherein crosslinking takes place by adding peroxides to the impregnation solution and operating at temperatures from 100° to 300°C.